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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Aqueous Emulsion Copolymers and Thickening Procedures Using Them.

We, ROHM & HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 222 West Washington Square, Philadelphia 5, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention is concerned with the production of novel aqueous dispersions of emulsion copolymers which have, besides other uses, capacity for thickening various systems, including organic solvent systems, and outstanding capacity for thickening aqueous dispersions of water-insoluble polymeric materials of either natural or artificial origin. The invention also relates to the use of the dispersions for various purposes and especially to the procedures for thickening aqueous systems using the copolymers of the present invention and the thickened systems thereby obtained.

Salts of polyacrylic acid and polymethacrylic acid have heretofore been used as thickeners in various aqueous systems. Products useful for this purpose have also been made by the hydrolysis of polymerized esters, amides or nitriles of acrylic acid.

Generally, hydrolysis of at least 60% of the acid derivative groups in the polymer was necessary to impart water-solubility to the hydrolysis product. The customary practice was to hydrolyze 70 to 90% or more of the ester, nitrile or amide groups usually with sodium or potassium hydroxides. Hydrolysis products of this character are generally produced in concentrations of 5 to 15% in water, and, because of the difficulty and expense of drying the viscous product, they are generally sold and distributed in this aqueous form. Because of the extremely high viscosity of such hydrolysis products, it has been necessary to dilute the aqueous solutions thereof to a concentration of approximately 5% before the viscosity is sufficiently lowered to assure adequate miscibility thereof with the aqueous dispersion to be thickened in simple agitating and mixing equipment. Thus, in using such hydrolysis products, 19 parts of water is added for each part of the effective thickening agent during the incorporation of the 5% solution into the aqueous dispersion to be thickened. It is obvious that the use of such dilute solutions cannot be expected to produce the maximum increase in viscosity for a given weight of polymeric material.

United States Patent 2,123,599 has already

suggested the copolymerization of water-insoluble derivatives of acrylic acid or methacrylic acid, such as the esters or nitriles thereof, by a technique which involves the emulsification of the monomers in an aqueous medium. In some cases, artificial latices are obtained, but, when ethyl acrylate was copolymerized with acrylic acid, it is stated to have produced a hard elastic mass. British Patent 426,265 discloses the preparation of aqueous dispersions of copolymers containing up to about 15% of acrylic acid by emulsification of the monomers in an aqueous system and polymerizing by adding suitable catalysts or initiators. Copolymers containing such small amounts of acrylic acid, however, though increasing the viscosity of systems to which they are added and then neutralized with an alkaline material, such as sodium hydroxide, have limited capacities for increasing the viscosity of the aqueous systems to which they are added. In addition, concentrations of the acrylic acid copolymer must be greatly reduced, such as less than 20%, when greater than 15% of acrylic acid is attempted to be introduced into the copolymer by emulsion copolymerization technique. Otherwise, coagulation to hard elastic masses, as in U.S. Patent 2,123,599, occurs. U.S. Patent 2,326,078 discloses the production of a copolymer of methyl methacrylate with at least 40% of methacrylic acid in granular form. The patentee states that this composition represents the smallest amount of the methacrylic acid which can be employed to yield a copolymer soluble in aqueous solutions of sodium or potassium hydroxide.

U.S. Patent 2,244,703 suggests emulsion copolymerization of 80 to 98% of methacrylic acid with esters of such acid. However, it has been found that when such large amounts of the acid are used in admixture with methacrylic acid esters, in emulsion copolymerization procedures, stable copolymer dispersions are not obtained unless the solids concentration is kept well below 25%, such as about 15%. This limits the efficiency of the system and increases the cost, especially when transportation over considerable distances is required. Even more important is the fact that when such polymers are solubilized they give low aqueous viscosity and poor thickening efficiency in latex and pigment systems.

In accordance with the present invention, there is provided a stable aqueous dispersion of a water-insoluble emulsion copolymer containing 25 to 70% by weight of methacrylic acid, at least 10% by weight of a copolymerized lower acrylate component constituted by one or more copolymerized acrylic acid esters of C_1-C_4 alcohol, and 0 to 40% by weight of one or more other copolymerized neutral monoethenically un-

saturated monomers, the dispersion containing a dispersing agent and having a solids concentration of 25% to 50% by weight.

The dispersions of the invention, whilst having a fairly high concentration of solids, are mobile liquids and are thus readily adapted to be added directly to systems to be thickened.

The lower acrylate or a mixture thereof may make up the entire balance of the emulsion copolymer (i.e. that portion not derived from methacrylic acid) or a portion of the balance (up to 40% by weight of the copolymer) may be derived from any other neutral monoethenically unsaturated copolymerizable monomer or mixture thereof, methyl methacrylate being preferred. It is essential that the copolymers contain at least 10% of a lower acrylate in any case. Besides imparting stability, it appears that the introduction of the lower acrylate serves to make the copolymer insoluble in the free acid form yet soluble in alkaline media, such as sodium or potassium hydroxide, even though there may be less than 40% methacrylic acid in the copolymer, the low limit of alkali-solubility set in U.S. Patents 2,244,703 and 2,326,078. This is quite an advantage since it renders useful and for the thickening of aqueous systems such copolymers which contain less than 40% methacrylic acid, such as 25% or 38%. Preferably, the emulsion copolymer contains no more than 50% by weight of copolymerized methacrylic acid because, if the proportion of methacrylic acid is increased beyond 50%, such as up to 60 or 70% or more by weight of the copolymer, the increased proportion of the acid reduces the efficiency of the salt of the copolymer in thickening some polymeric dispersions. Furthermore, as the proportion of methacrylic acid is increased beyond about 50%, the upper limit of concentration of the polymeric solids in the emulsion copolymerization system must be generally progressively lowered in order to obtain a stable dispersion. Consequently, such copolymer systems having increased acid content have the additional disadvantage of reduced concentration.

Surprisingly, copolymers containing 25 to 50% of methacrylic acid and at least 10% of lower acrylate units, especially of ethyl acrylate, with or without another comonomer, such as methyl methacrylate, are capable of producing an increase in viscosity in certain aqueous dispersions to be thickened, especially water-insoluble polymer latices, from two to ten times the amount obtained by commonly used thickeners, based on the hydrolysis of polyacrylonitrile, when used in corresponding amounts on the basis of thickener solids added. Examples of the lower acrylates include methyl, ethyl, propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, and *t*-butyl acrylates. Examples of the other

monomers include any other acrylate, any ester of methacrylic (particularly methyl or butyl methacrylate) or itaconic acids, vinyl acetate, vinyl chloride, acrylonitrile, methacrylonitrile and styrene.

The advantages of using the aqueous emulsion copolymers of the present invention as compared to the polymeric thickeners conventionally used heretofore include lower cost of manufacture, excellent reproducibility, high solids content which minimizes transportation cost, and high capacity of thickening a variety of systems on neutralization. The aqueous emulsion copolymers of the present invention are also rapidly solubilized by neutralization with bases, including ammonia, alkali metal hydroxides, such as sodium, potassium or lithium hydroxide, water-soluble amines such as methylamine, trimethylamine, ethylamines, monoethanolamine, diethanolamine, triethanolamine, morpholine and piperidine. The fact that the emulsion copolymer is prepared and may be shipped in the acid form allows the user to prepare rapidly whatever salt is required for his particular application. This versatility is not present in the conventional water-soluble thickeners which are supplied in salt form.

The emulsion copolymers of the present invention generally have a molecular weight of at least 100,000 and may have a molecular weight as high as several million. The emulsifier may be used in a proportion of $\frac{1}{4}$ to 6% of the weight of monomers. They may be produced by conventional aqueous emulsion polymerization techniques using appropriate emulsifying or dispersing agents for emulsifying the monomers and for maintaining the polymer obtained in dispersed condition. Preferably, water-soluble initiators are used such as the alkali metal or ammonium persulfates in amounts from 0.10 to 3% on the weight of the monomers. Preferably, too, a redox system is used in which the persulfate or like initiator is used in conjunction with a reducing agent such as sodium metabisulfite in about the same proportion as the initiator. A promoter, such as small proportions of metal ions, such as copper or iron, may be used. The polymerization may be effected as a batch system or by continuous addition of the monomers to the aqueous solution containing initiator, reducing agent and promoter. Generally, it is unnecessary to heat the polymerization system, and in many cases it may be desirable to cool the system to control the temperature and maintain it between room temperature and 85° C. Agitation during the polymerization is generally desirable but may be omitted. The amount of water may be selected at the beginning of the polymerization procedure with reference to the amount of comonomers to be copolymerized so that any desired

concentration on the order of 25 to 50% or more of copolymer is obtained in dispersed condition in the reaction vessel. The copolymer dispersion thereby obtained may be directly transported, or sold and shipped, to a point at which it is to be used for thickening or other purposes.

Examples of emulsifiers that may be used include the alkali metal salts of higher alkyl sulfates, such as sodium lauryl sulfate or sodium α -hydroxy octadecane sulfonate.

The dispersions of the present invention may be used for thickening many aqueous systems, such as other emulsion copolymer dispersions obtained by emulsion polymerization, natural rubber latices as well as synthetic rubber latices, aqueous coating compositions for the paper, leather, and textile industries, water-base paints, including those using aqueous dispersions of emulsion-polymerized vinyl or acrylic monomers, drilling muds, waxes, polishes, pigment suspensions, cosmetics and toiletries, food products and pharmaceuticals.

Among the latices and aqueous dispersions of vinyl and acrylic polymers that are obtained by emulsion polymerization and may be thickened by the use of the dispersions of the present invention are copolymers of styrene with butadiene, similar copolymers of acrylonitrile with butadiene, homopolymers of styrene, homopolymers of vinyl chloride, copolymers of 75 to 95% vinyl chloride with 25 to 5% of vinylidene chloride, acrylonitrile or vinyl acetate, polychloroprene, vinyl acetate homopolymers and copolymers, homopolymers and copolymers of acrylic acid esters or methacrylic acid esters, such as those of alcohols having one to eight carbon atoms listed hereinabove, also copolymers of the acrylic acid esters or methacrylic acid esters with vinyl chloride, vinyl acetate, acrylonitrile, styrene or the like.

The aqueous dispersions of these water-insoluble polymers may contain emulsifiers of anionic and non-ionic type. Suitable anionic emulsifiers that may be present include the higher fatty alcohol sulfates such as the sodium or potassium salts of the sulfates of alcohols having from eight to eighteen carbon atoms, such as lauryl alcohol, alkali metal salts or amine salts of higher fatty acids such as those of fatty acids having from eight to eighteen carbon atoms with sodium, potassium, or any of the ethanolamines, such as triethanolamine, examples of which include triethanolamine oleate or stearate, rosin soaps, sulfonated compounds such as turkey red oil or sulfonated ricinoleic acid, and sulfonated alkylaryl compounds, such as sodium dodecyl benzene sulfonate and sodium *tert*-octylphenoxydiethoxyethanol sulfonate. Examples of non-ionic emulsifiers include alkylphenoxy polyethoxyethanols

having alkyl groups of about seven to eighteen carbon atoms and about nine to thirty or more oxyethylene units, such as heptylphenoxypolyethoxyethanols, octylphenoxypolyethoxyethanols, methyloctylphenoxypolyethoxyethanols, nonylphenoxypolyethoxyethanols and dodecylphenoxypolyethoxyethanols; polyethoxyethanol derivatives of methylene-linked alkyl phenols; sulfur-containing agents such as those made by condensing the required proportion of ethylene oxide with nonyl, dodecyl, tetradecyl, and the like mercaptans or with alkylthiophenols having alkyl groups of six to fifteen carbon atoms; ethylene oxide derivatives of long-chained carboxylic acids, such as lauric, myristic, palmitic and oleic or mixtures of acids such as found in tall oil; ethylene oxide condensates of long-chained alcohols, such as octyl, decyl, lauryl, or cetyl alcohols; and ethylene oxide derivatives of etherified or esterified polyhydroxy compounds having a hydrophobic hydrocarbon chain.

Besides being useful in thickening aqueous systems, some of the emulsion copolymers of the present invention, and especially those that are modified by light cross-linking as discussed hereinafter, may be used to thicken polar organic solvent systems. These copolymer dispersions, in which the copolymer is still in acid form, are effective thickeners for methanol, ethanol, ethylene glycol, acetone, dioxane, methyl ethyl ketone, the mono-ethyl and mono-butyl ethers of diethylene glycol, and 2-butoxyethanol and systems containing such solvents mixed with other solvents including water; while, in the sodium salt form, they are effective thickeners for methanol, ethanol, glycerol, ethylene glycol and mixtures thereof with other solvents, such as water. Thus, they may be used for thickening paint-removing solvent systems so that they do not run off inclined and especially vertical walls or other surfaces.

For some purposes the dispersion of the copolymer may be dried, such as by a spray-drying technique or a drum-drying technique (in which the film is spread as a thin film on a heated drum), whereby a powder is directly obtained which can then be dissolved or dispersed in any solvent desired, either of aqueous or non-aqueous organic type.

In many instances, the preferred method of application of the dispersions of the present invention for thickening purposes is to add the aqueous dispersion of the copolymer of methacrylic acid to the medium to be thickened and, after thoroughly mixing therein, to introduce an alkaline material to neutralize the acid copolymer. For some aqueous dispersions, it is preferred that there be present an alkaline material which automatically neutralizes the copolymer as it is introduced. Neutralization is fairly rapid after the copolymer dispersion has been

mixed in. The major portion of the thickening effect is obtained within a period of five to twenty minutes, although in some cases a small additional increase in viscosity may occur on standing longer.

Sufficient alkali may be employed to neutralize the acid copolymer completely or an excess thereof may be employed. However, it has been found in cases involving aqueous thickening that even greater thickening effects are frequently obtained when the proportion of alkaline material used is only sufficient to neutralize from 50 to about 75% of the carboxylic acid groups in the copolymer. This provides an additional way of obtaining a maximum thickening effect with a given amount of the thickening copolymer of the present invention. Of course, quite generally the degree of neutralization of the carboxylic acid groups in the copolymer must be such as to produce the desired thickening effect.

Alternatively, instead of adding the emulsion copolymer of the methacrylic acid to the system to be thickened and neutralizing subsequently or as a result of the presence of an alkaline material in the aqueous system being thickened, the aqueous copolymer may be neutralized in its dispersion before it is added to the system to be thickened. Generally, however, if this procedure is employed, the aqueous dispersion of the thickening copolymer should first be diluted to about a 5 to 15% solids concentration to facilitate the handling thereof and especially the intermixing of the aqueous dispersion of the copolymer salt obtained by neutralization with the systems to be thickened.

Preferably, the first procedure is employed wherein the dispersion of the copolymer of methacrylic acid before neutralization is added to the material to be thickened because an extremely high concentration, from 25 to 50%, of thickener solids can be employed and the compounder, in using such a high solids material, is handling a composition of low viscosity.

The copolymers hereinabove defined may further be modified by introducing a small proportion of a polyethylenically unsaturated copolymerizable monomer, such as divinylbenzene or diallylphthalate. Thus, from 0.1 to 0.8%, and preferably 0.1 to 0.5%, of such polyethylenically unsaturated compound may be introduced, based on the total weight of monomers. When this procedure is employed, there is a very low degree of cross-linking which, in effect, greatly increases the molecular weight and thickening efficiencies of the methacrylic acid copolymers in many systems. It is believed that the resulting polymer molecules are either highly branched or probably in the form of three-dimensional networks. In the sodium salt form, these networks swell several hun-

dred-fold and the consequent "micro-gel" structure acts as a highly efficient thickener. The cross-linking procedure is particularly applicable to copolymers containing 25 to 50% by weight of methacrylic acid, at least 10% of a lower alkyl ester of acrylic acid, and 0-40% of another neutral comonomer, such as methyl methacrylate. If proportion of methacrylic acid is increased to 60 or 70%, then, as before with the linear copolymers, this results in the disadvantage that it is necessary to lower the polymer solids in the emulsion to attain satisfactory stability. The preparation of the copolymers using a cross-linking agent is effected in the same general manner as described hereinbefore, except for the additional incorporation of the appropriate proportion of cross-linking agent. While the broad range of the proportion of the cross-linking agent is from 0.1 to 0.8% by weight, the optimum benefits are obtained for many cross-linking agents in the range of 0.15 to 0.3%, as is the case when diallyl maleate and diallyl phthalate are used. The examples of cross-linking agents that may be used include any copolymerizable compound which contains two or more non-conjugated points of ethylenic unsaturation or two or more non-conjugated vinylidene groups of the structure, $\text{CH}_2=\text{C}=\text{}$, such as divinyltoluene, divinylbenzene, trivinylbenzene, divinyl-naphthalene, ethylene glycol diacrylate or dimethacrylate, trimethylene glycol diacrylate or dimethacrylate, 2-ethylhexane-1,3-dimethacrylate, divinylxylene, divinylethylbenzene, divinyl ether, divinyl sulfone, allyl ethers of polyhydric compounds such as of glycerol, pentaerythritol, sorbitol, sucrose and resorcinol, divinylketone, divinylsulfide, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl phthalate, diallyl succinate, diallyl carbonate, diallyl malonate, diallyl oxalate, diallyl adipate, diallyl sebacate, diallyl tartrate, diallyl silicate, triallyl tricarballoylate, triallyl aconitate, triallyl citrate, triallyl phosphate, N,N^1 -methylenediacrylamide, N,N^1 -methylenedimethacrylamide, N,N^1 -ethylidenediacrylamide and 1,2-di-(α -methylmethylenesulfonamide)-ethylene.

When the cross-linked copolymers are employed, they may be applied for thickening by the same two general procedures described hereinabove. As before, the preferred procedure involves the addition of the copolymer still in the acid condition so that the dispersion thereof is of quite low viscosity to the system to be thickened, which either contains the neutralizing agent or to which the alkaline neutralizing agent is later added. However, if for any reason in a particular system it is preferred to neutralize the copolymer before adding it to the system to be thickened, it is preferable to dilute the aqueous emulsion copolymer thickener to a

solids concentration of 5% or less before neutralization to facilitate handling and intermixing with the system to be thickened.

It appears that one of the main reasons for the higher thickening efficiencies of the cross-linked copolymers in many systems is attributable to the higher molecular weight. The cross-linked copolymers of the present invention are especially advantageous for thickening aqueous systems which contain rather large proportions of wetting and/or dispersing agents, such as in highly stabilized latices either of natural rubber, synthetic rubber, or of vinyl or acrylic monomers. The cross-linked copolymers are also especially effective in thickening low solids (e.g., 10 to 20%) systems or water itself. The use of the linear type of thickeners in pigment suspensions often results in a flocculation effect with resulting separation, whereas the use of the cross-linked polymer thickeners of the present invention is generally free of any flocculating tendencies. These lightly cross-linked materials are unique in the water-soluble polymer field in regard to their suspending action for pigments, abrasives, ceramics, etc. Unlike conventional polyacrylate or natural gum thickeners, it is possible with the lightly cross-linked emulsion copolymers of the present invention to thicken suspensions of pigments to relatively low viscosities (500 to 100 cps., Brookfield 12 R.P.M., 25° C.) and yet obtain stability in the suspension as measured by lack of separation.

A pronounced advantage of the cross-linked modification is that the aqueous thickening obtained by the use of a given proportion of the thickening copolymer is relatively independent of temperature as compared to the linear copolymer thickeners of the present invention which tend to manifest reduction in viscosity as the temperature increases. This independence of viscosity on temperature is also observed in many latex, compounded latex, and pigment dispersions. For example, in aqueous synthetic emulsion polymer paint systems which are used in hot climates or during hot weather or in other elevated temperature environments, use of the cross-linked thickeners is highly advantageous.

The proportion of the thickener (linear or micro-gel) that may be employed in any given system may fall within a wide range, depending upon the particular system and its concentrations. As little as 0.1% (by weight, based on total weight of solids in the system to be thickened) of thickener copolymer solids may be adequate for many purposes. On the other hand, for some systems, it may be desirable to use as much as 5% or more of the thickener copolymer. Generally, the use of from 0.5 to 2% of the thicker copolymer is adequate for most thickening purposes.

The ammonium salts of both the linear and cross-linked copolymers of the present invention are also useful as binders for ceramics. Along with good binding properties in this application, they have low ash content on burning out, being on the order of about two-thirds of a per cent. The ash content of the polymer dispersion can be further reduced to as low as about 0.04% or less by treatment with a mixture of cation-exchange and/or anion-exchange resins.

The copolymer dispersions of the present invention are also useful for the production of water-insoluble coatings or films. For this purpose, the acid form of the emulsion copolymers in their aqueous dispersion may be converted to the ammonium salt and then zinc ammonium complex salts are added. This provides a solution of the copolymer which can be applied to surfaces to be coated or impregnated from the aqueous medium and which dry to produce a clear, colorless, water-insoluble film.

While anion, i.e. water-soluble polymers of high molecular weight are not prime flocculants for aqueous suspensions of suspended solids, such as of inorganic or organic materials, including minerals and ores, they do act as flocc-stabilizers. That is, if a system is put in the flocculated state by the addition of salt or some other means, the addition of anionic polymers will then serve to stabilize and increase the size of the flocs. This results in increased settling and filterability of the suspension. The copolymer dispersions herein described exhibit this flocc-stabilization property. Compared to conventional acrylic thickeners, the dispersions of the present invention have the added advantage that they can be added directly in the acid form to alkaline suspensions to give in situ "floc-stabilization."

The lightly cross-linked copolymer dispersions of the present invention may be added to all sorts of coating compositions of aqueous type, such as aqueous dispersions of water-insoluble emulsion copolymers, hydrophilic colloids, such as polyvinyl alcohols, hydrolyzed or partially hydrolyzed polyvinyl acetates, and the like which are of alkaline character. The addition of the cross-linked copolymer dispersions of the present invention to such systems renders the systems quite thixotropic and imparts short flow. This is useful when the compositions are intended to be applied to porous substrates and it is desired to have a relatively low penetration of such substrate. For example, in coating compositions intended to be applied to textile fabrics, such as printing pastes, the application of such pastes such as by passage through rolls is such that the shear of the roll sets the layer in position on the fabric without causing excessive penetration of the fabric. The cross-linked copolymer disper-

sions are especially valuable in the preparation of aqueous alkaline systems for the finishing, filling, rug backing and pigment-printing and dyeing of textile fabrics.

The use of small amounts of high molecular weight polyelectrolytes as soil conditioners is well known. The addition of 0.01 to 0.5% of these polymers to soil results in the formation of soil aggregates which are stable to the action of rainfall. This prevents the surface-slaking of soil with consequent increase in seed emergence rate. Previous work has described the use of either solution or solid forms of polyelectrolytes to achieve this soil-conditioning effect. The solution form has the disadvantage of low solids and high viscosity and also the extreme difficulty of uniformly incorporating the polymer into the soil. The powdered forms are relatively slow to dissolve in the soil water. They present a severe dusting problem, and they are also difficult to incorporate uniformly. The copolymer dispersions of the present invention are admirably suitable for conditioning soils having pH values above seven. They are substantially lower in cost than previously-described materials and they can be uniformly incorporated into the soil with ease since they are applied to alkaline soils as appropriately diluted water-thin dispersions and act as "in situ" soil conditioners. The alkaline soils present in arid regions are particularly amenable to treatment by these polymers.

The copolymer dispersions of the present invention are useful as additives for drilling muds. The copolymers herein described are useful water-loss control agents and, since all commercial drilling fluids are alkaline, it is possible to add the copolymer dispersions in the acid form directly to the alkaline clay dispersion, that is, the drilling mud, where the copolymers are then solubilized by the alkalinity and serve to reduce the water-loss when the drilling mud contacts porous structures. For this purpose, lower molecular weight polymers such as those made in the presence of a chain transfer agent are generally preferred.

In the following examples which are illustrative of the invention, the parts and percentages are by weight unless otherwise specifically indicated and, unless otherwise noted, the viscosities are in centipoises and determined with a Brookfield viscosimeter at 12 R.P.M. and 25° C. The emulsifiers used are as follows:—

Emulsifier A—Sodium α - hydroxy - octadecane-sulfonate.

Emulsifier B—Sodium lauryl sulfate.

Emulsifier C—*t*-Octylphenoxypolyethoxyethanol containing about ten oxyethylene units.

EXAMPLE 1.

The following are added to a reaction vessel:

Water	900 c.c.
5 Solution of 0.25 gram $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 500 c.c. water	75 c.c.
<i>t</i> -Butyl hydroperoxide	0.3 c.c.

10 An aqueous emulsion is prepared by agitating together in a separate vessel the following:

Aqueous Emulsifier B (27%)	111 grams
Deionized water	1020 c.c.
Ammonium persulfate	3 grams
Ethyl acrylate	750 grams
15 Butyl methacrylate	255 grams
Methacrylic acid	495 grams

To the reaction vessel, there is then added 450 grams of the monomer emulsion, the temperature of the contents being then adjusted to 20° C., and 0.8 gram of sodium metabisulfite is then added. The temperature rises and levels off at about 50° C. Then additional monomer emulsion is added at a rate of 222 grams every ten minutes and concurrently a solution of 3.75 grams of sodium metabisulfite in 150 c.c. of water is added at a rate of 15 c.c. every ten minutes until all of the emulsion and metabisulfite are added. The total time of polymerization (during which the temperature is maintained at 50° to 56° C. by cooling) amounts to 110 minutes, at which time about ten drops of *t*-butyl hydroperoxide are added and the reaction mixture is stirred another half hour. After cooling to 30° C., the dispersion is filtered. The filtrate provides an approximately 40% solids emulsion copolymer dispersion (substantially 100% yield) in which the copolymer composition is approximately 33% methacrylic acid, 17% butyl methacrylate, and 50% ethyl acrylate.

This polymer is solubilized after dilution with water by addition of an equivalent amount of NaOH. This instantaneously gives a clear solution. A 5% solution of the salt has a viscosity of 1600 cps. and a pH of 8.0.

EXAMPLE 2.

50 An aqueous dispersion containing about 29% of a copolymer of about 40% methacrylic acid, about 60% ethyl acrylate, and 0.20% of diallyl maleate is prepared as follows:

55 An aqueous emulsion is made by mixing together the following:

Deionized water	835 ml.
Aqueous Emulsifier B (27%)	30 grams
Ethyl acrylate	324 grams
Methacrylic acid	216 grams
Diallyl maleate	1.08 grams
Ammonium persulfate	1.35 grams

60 One hundred and thirty grams of this monomer emulsion and 470 c.c. of deionized water are charged into a glass reaction vessel and are heated to about 90° C. When refluxing stops, the remaining monomer emulsion is introduced at a rate of about 18 grams/minute. After addition is completed, the dispersion is maintained at about 90° C. for 15 minutes. Then it is cooled to room temperature and filtered through cheese cloth to remove minute traces of gum.

The above polymer dispersion is diluted and an equivalent amount of sodium hydroxide is added. This instantaneously gives a clear solution which has a 5% viscosity of 45,600 cps. and a pH of 7.9.

EXAMPLE 3.—

A variety of copolymer dispersions are prepared in a manner similar to that described in Example 1. These are then diluted and converted to the sodium salt by addition of one equivalent of NaOH and the thickening properties of the sodium salts are determined. The results are given in TABLE I, wherein EA is ethyl acrylate, MMA is methyl methacrylate, MAA is methacrylic acid, BMA is butyl methacrylate, MA is methyl acrylate, and ST is styrene. Latex A is a commercially available synthetic rubber latex made by the "hot" process of a copolymer of butadiene and containing about 46% bound or copolymerized styrene to which 1% (on weight of copolymer) of emulsifier C is added as a stabilizer. The viscosity is measured after 2% (on weight of copolymer) of thickener copolymer solids is added, the final latex, the viscosity of which is given in the table, having about 20% solids concentration after such additions. Without the addition of thickener copolymer, the latex has a viscosity of four centipoises and a pH of about ten. Latex B is a dispersion of clay in Latex A (without thickener) such that the ratio of copolymer solids to clay is 1:1 and the butadiene-styrene solids concentration is about 10%. The viscosity given in the table is that measured after the addition of 5.0% of thickener copolymer solids (on weight of butadiene-styrene copolymer solids), at which time the butadiene-styrene copolymer solids is 10.0%. Without the thickener, Latex B has a viscosity of three centipoises and a pH of about 11.

TABLE I.

Copolymer Dispersion *						Sodium Salt				
5	Components Weight %			Emulsifier % on Monomers		Solids	1% Solution in water		Viscosity	
	MAA	EA	Other			%	pH	Visc.	2% in Latex A	5% in Latex B
10	30	60	10 MMA	2	B	41.1	7.75	84	—	1300
	33	50	17 MMA	2	B	40.0	7.7	74	9300	7000
	40	20	40 MMA	4.3	B	26.5	8.1	515	1210	2640
	40	60	0	2	A	35.3	8.0	315	5480	7000
	50	25	25 MMA	1.5	B	33.5	7.6	625	710	—
15	33	50	17 BMA	2	B	41.1	8.0	77	—	5200
	33	50	17 ST	2	B	41.0	8.3	24	—	2880
	28	36	36 MA	2	B	29.6	7.8	68	—	5920
	NaPAN _y				—	12.5	8.6	101	545	250

Note *—All copolymers are believed to have viscosity average molecular weights substantially in excess of 100,000. E.g., the second in the table has an intrinsic viscosity of 1.34 deciliter per gram in acetone corresponding to an estimated viscosity average molecular weight of 800,000.

Note y—Sodium salt of 70% hydrolysed polyacrylonitrile included in the table as representative of a conventionally available thickener for comparative purposes.

EXAMPLE 4.

A series of cross-linked emulsion copolymer dispersions are prepared in a manner similar to that described in Example 2, using 2% emulsifier A and diallyl phthalate instead of diallyl maleate. These polymer dispersions are diluted and are then converted to the sodium salts by addition of an equivalent amount of NaOH and the thickening properties of the salts are determined in

their own 1% and 5% aqueous solutions and when added to Latex C, a butadiene-acrylonitrile copolymer dispersion (having a viscosity of 3 cps. when diluted to 20% solids and pH of about eight before addition), the amount of thickener copolymer being 5% solids on the weight of acrylonitrile copolymer solids, and the final concentration of the latex being 20%. The results are given in Table II.

TABLE II.

50	Copolymer Dispersion		Sodium Salt			
	Cross- Linker	Solids %	5% Solution in water		1% Solution in water	5% in Latex C
			pH	Visc.	Visc.	Visc.
55	None	25	8.0	—	50	670
	0.10	25	8.0	890	144	1340
	0.20	25.6	8.1	16,900	1460	4720
	0.30	25	8.0	30,600	2640	4000
	0.40	25	7.9	>50,000	4360	2280
55	0.50	25	8.4	>50,000	2120	390
	0.65	25	8.2	>50,000	940	140

Example 5.

A series of cross-linked emulsion copolymer dispersions are prepared, using 1.5% emulsifier B or 3% of emulsifier A as indicated and different cross-linkers in a manner similar to Example 2, except the last, which is made in a manner similar to Example 1.

All copolymers are 60/40/EA/MAA weight ratio and contain 0.10 or 0.20% of the cross-linker. They are converted to the sodium salts and tested for thickening on latex C as in Example 4. Table III gives the following results:

TABLE III.

Copolymer Dispersion				Sodium Salts			
Cross-Linker		Emulsifier	Solids %	5% Solution in water		1% Solution in water	5% in Latex C
Type	%			pH	Visc.	Visc.	Visc.
Polyallyl ether of sucrose (6.2 allyl groups per molecule)	0.20	B	29	7.8	29,800	3460	3480
Diallyl maleate	0.20	B	29	7.9	45,600	4920	3800
Diallyl phthalate	0.20	B	28	7.6	29,900	3100	4260
Trimethylene glycol diacrylate	0.10	A	26	8.0	>50,000	2100	2660

Example 6.

A series of cross-linked emulsion copolymer dispersions are prepared containing varying methacrylic acid content. All of these contained 0.20% diallyl phthalate and

1.5% Na lauryl sulfate as the emulsifier. BA is butyl acrylate. Their viscosities and thickening effect on Latex C are determined as in Example 4.

TABLE IV.

Copolymer Dispersion				Na Salt			
EA	Weight % BA	MAA	% Solids	5% Solution in water	1% Solution in water	5% in Latex C	
				pH	Visc.	Visc.	Visc.
75	—	25	28	7.9	23,900	1620	3060
67	—	33	28	8.2	16,400	1640	4240
50	—	50	25	8.2	24,000	2820	4200
40	—	60	21	8.1	15,800	1840	3420
—	60	40	29	8.3	40,000	960	3800

EXAMPLE 7.

(a) A 40% aqueous dispersion of a copolymer of 50% EA, 17% MMA and 33% MAA (second in TABLE I) is diluted to 5% concentration, neutralized with NaOH and then added to several portions of various latices in different amounts until the viscosity is raised to 2000 cps., 6000 cps., and 10,000 cps., respectively. The percentage added is given below on the basis of thickener copolymer solids on total solids of the

system to be thickened. In 50% solids natural rubber latex, the percentages needed to give the viscosities above are 0.6%, 2.2%, and 3.5%. In a 39% aqueous dispersion of the potassium salt of a copolymer of 67% EA, 31.7% MMA, and 1.3% MAA, the amounts of thickener added are 0.8%, 2.6%, and 3.7%. The amounts of thickener added to a 60% aqueous dispersion of rutile TiO₂ dispersed with 0.25% of the sodium salt of a copolymer of maleic anhydride and diiso-

butylene are 0.5%, 1.2%, and 1.7%, respectively. The amounts added to give viscosities of 2000 and 6000 cps. in a 35% solids dispersion in water of a mixture of one part of TiO_2 , four parts of clay, and 0.7 part of the potassium salt of a copolymer of 87% EA, 10.5% MMA, and 2.5% of itaconic acid are 3.2% and 5%, respectively.

(b) An approximately 28% aqueous dispersion of a copolymer of 60% EA, 40% MAA, and 0.20% (on eight of EA and MAA) of diallyl phthalate is diluted to 5% concentration, neutralized with NaOH and then added to several portions of various latices in different amounts until the viscosity is raised to 2000 cps., 6000 cps., and 10,000 cps., respectively. The percentage added is given below on the basis of thickener copolymer solids on total solids of the system to be thickened. In 50% solids natural rubber latex, the percentages needed to give the viscosities above are 0.8%, 1.3%, and 1.6%. In a 39% aqueous dispersion of the potassium salt of a copolymer of 67% EA, 31.7% MMA, and 1.3% MAA, the amounts of thickener added are 1.0%, 1.3%, and 1.6%, respectively. The amounts of thickener added to a 60% aqueous dispersion of rutile TiO_2 dispersed with 0.25% of the sodium salt of a copolymer of maleic anhydride and diisobutylene are 0.3%, 0.5%, and 0.6%, respectively. The amounts added to give viscosities of 2000 and 6000 cps. in a 35% solids dispersion in water of a mixture of one part of TiO_2 , four parts of clay and 0.7 part of the potassium salt of a copolymer of 87% EA, 10.5% MMA, and 2.5% of itaconic acid are 1.4% and 1.9%, respectively.

EXAMPLE 8.

To 83 parts of a 60% solids natural rubber latex, there are added 12.7 parts of H_2O , 0.3 part of 28% ammonium hydroxide, and 4.0 parts of a 28% dispersion in water of an emulsion copolymer of 60% EA, 40% MAA, and 0.20% (on total EA and MAA) of diallyl phthalate. The latex obtained has 50% total solids and a viscosity of 24,000 cps.

EXAMPLE 9.

To 82 parts of a dispersion in water of rutile TiO_2 (12.2% solids), there are added 15.1 parts of 1% sodium hydroxide solution and 2.9 parts of a 28% aqueous dispersion of an emulsion copolymer of 60% EA, 40% MAA, and 0.25% (on total of EA and MAA) of diallyl phthalate. The final dispersion has a 10% pigment solids content and a viscosity of 2840 cps. and contains 9% of the thickener (based on sodium salt form) on the weight of pigment solids.

EXAMPLE 10.

The 28% aqueous dispersion of cross-linked copolymer of Example 9 is diluted to 5%

solids and neutralized with NaOH. The salt solution is then added to the initial rutile TiO_2 dispersion of Example 9 until 9% of the salt on the weight of pigment solids has been introduced. The final concentration of the pigment dispersion is 10% pigment solids and it has a viscosity of 2800 cps.

EXAMPLE 11.

To 87 parts of a 45% aqueous dispersion of a copolymer of 67% EA, 31.7% MMA, and 1.3% of the NH_4 salt of MAA, there are added 0.1 part of 28% ammonium hydroxide and 0.9 part of a 40% aqueous dispersion of an emulsion copolymer of 60% EA and 40% MAA diluted with twelve parts of water. The final dispersion has a pH of 7.0, a solids content of about 39%, and a viscosity of 6100 cps. and contains 1% of the 40% MAA copolymer (based on its ammonium salt) on the weight of the first copolymer.

EXAMPLE 12.

The 40% aqueous dispersion of Example 11 is diluted to 5% solids concentration and neutralized with ammonium hydroxide. The salt solution obtained is then added to the 45% aqueous dispersion of Example 11 until 1% of the salt (on the weight of 1.3% MAA copolymer solids) is introduced, and the final latex solids is adjusted to 39%. The final dispersion has a pH of 6.8 and a viscosity of 7100 cps.

EXAMPLE 13.

(a) Eighteen parts of an emulsion copolymer dispersion, of 28% solids consisting of 60 parts of EA with 40 parts of MAA, cross-linked by 0.2% of diallyl phthalate, is added to 82 parts of the monoethyl ether of diethylene glycol, yielding a viscosity of 6200 cps. Eighteen parts of the same acid emulsion copolymer dispersion in 82 parts of the monobutyl ether of diethylene glycol yields a viscosity of 6680 cps. The introduction of 18 parts of the same acid emulsion copolymer dispersion in 82 parts of 2-butoxy-ethanol yields a viscosity of 3120 cps.

(b) One per cent of the sodium salt of the same copolymer in a mixture of 39 parts of ethanol with 50 parts of water yields a viscosity of 2400 cps. and at the level of 1% in a mixture of 62 parts of glycerol with 50 parts of water yields a viscosity of 5000 cps.

EXAMPLE 14.

(a) A 10% aqueous dispersion of an anionically dispersed, paint grade, fine-particle size (0.4 micron), rutile TiO_2 of pH 10 is thickened with 0.54% (based on total suspension) of the sodium salt of the copolymer of Example 13 to give a viscosity of 950 cps. This suspension shows no separation on storage for 60 days. When other conventional thickeners are used in amounts

to attain 950 cps. in such a suspension, the suspensions show separation.

- (b). A 10% aqueous dispersion of anionically dispersed, 2-micron, filler grade, calcium carbonate having a pH of 9.5 is thickened with 0.36% (based on total suspension) of the sodium salt of Example 13 to give a viscosity of 151 cps. This suspension shows no separation after fourteen days, whereas the same suspension without thickeners had completely settled during the fourteen day period.

EXAMPLE 15.

Preparation of Insoluble Coating or Film.

- To 24 parts of a 50/17/33 EA/MMA/MAA dispersion having 40% solids concentration are added 73.8 parts of water and 2.2 parts of 28% ammonia. To this solution there is added a solution containing four parts of the dihydrate of zinc acetate and 4.4 parts of 28% ammonia. The pH is adjusted to about 9.5 with ammonium hydroxide. The solution is coated on glass, wood, steel, aluminium, and leather panels and dried, yielding in every case a water-insoluble coating on the respective substrate.

EXAMPLE 16.

Aid for Filtration and Sedimentation.

- The settling rate and filtration time are determined by a suspension containing 10 grams of kaolin per 100 c.c. in 0.18 N sodium chloride at a pH of 7.6. Whereas the kaolin suspension without any addition settled at the rate of 0.042 cm. per second and required a total filtration time of 710 seconds, the incorporation into the suspension of the copolymer dispersion of Example 15, with the copolymer in the sodium salt form, so as to provide 0.1% of the copolymer on the weight of the clay, increases the settling rate to 0.067 cm. per second and reduces the filtration time to 125 seconds. The introduction of 0.1% (on weight of kaolin) of the sodium salt of the copolymer of Example 13 increased the settling rate to 0.26 cm. per second and reduced the filtration time to 335 seconds.

EXAMPLE 17.

Soil Conditioning.

- An alkaline soil (a 50% aqueous suspension of which has a pH of 10.4) containing about 20% sand, 60% silt, and 20% clay is sprayed with a 0.3% solids dispersion of the copolymer of Example 15 in the acid form in such an amount that the soil sample contains 77% moisture and 0.10% polymer on the weight of the soil. The soil sample is tested for aggregate stability as described by Hedrick and Mowry (Soil Sci., 73, 427-441, 1952). After 24 hours, the soil is pressed together and passed through a 4-mesh screen to form crumbs. The crumbs are dried and then wet-sieved for 30 minutes by the method of Yoder (J. Am. Soc.

Agr. 28, 337-351, 1936). Whereas, without the addition of the polymer, only 12.5% of the soil was of a size greater than 0.25 mm., with the polymer addition, 73% of the soil had greater than 0.25 mm. size.

EXAMPLE 18.

Drilling Mud.

In a typical well-drilling operation wherein the water loss amounted to 18 c.c. within 15 minutes with a typical "red mud" containing 17.55 lbs./barrel of clay (4 parts low yield clay to 1 part sodium bentonite), 2.5 pounds NaOH, 3.0 lbs./barrel quebracho, 5.0 lbs./barrel calcium hydroxide, the slurry having a pH of 12.3, the addition of one lb./barrel of the sodium salt of the copolymer of Example 13 reduced the water loss to a rate of 6.0 c.c. in 15 minutes and the addition of one lb./barrel of the sodium salt of the copolymer of Example 15 reduces the water loss to a rate of 7.0 c.c. per 15 minutes.

WHAT WE CLAIM IS:-

1. A stable aqueous dispersion of a water-insoluble emulsion copolymer containing 25 to 70% by weight of methacrylic acid, at least 10% by weight of a copolymerized lower acrylate component constituted by one or more copolymerized acrylic acid esters of a C₁-C₄ alcohol, and 0 to 40% by weight of one or more other copolymerized neutral monoethylenically unsaturated monomers, the dispersion containing a dispersing agent and having a solids concentration of from 25% to 50% by weight.

2. A dispersion according to Claim 1 wherein the copolymer contains not more than 50% by weight of copolymerized methacrylic acid.

3. A dispersion according to Claim 1 or 2 in which the lower acrylate component is constituted by copolymerized ethyl acrylate.

4. A dispersion according to Claim 1 or 2 in which the lower acrylate component is constituted by copolymerized butyl acrylate.

5. A dispersion according to any one of Claims 1-4, wherein the copolymer is composed entirely of copolymerized methacrylic acid and said lower acrylate component.

6. A dispersion according to any one of Claims 1-4, wherein the copolymer contains units from at least one other neutral monoethylenically monomer, which units are derived from one or more of the following, viz. esters of acrylic acid (other than C₁-C₄ alcohol esters), esters of methacrylic acid, esters of itaconic acid, vinyl acetate, vinyl chloride, acrylonitrile, methacrylonitrile and styrene.

7. A dispersion according to any one of Claims 1-4, wherein the copolymer consists of copolymerized (1) methacrylic acid, (2) said lower acrylate component, and (3) methyl methacrylate.

8. A dispersion according to any one of the preceding claims containing, as dispersing agent, $\frac{1}{2}$ to 6% by weight, based on the copolymer, of at least one anionic or non-ionic emulsifier.

9. A dispersion according to any one of the preceding claims, except that the copolymer also contains from 0.1 to 0.8% by weight of copolymerized polyethylenically unsaturated cross-linking agent.

10. A dispersion according to Claim 9, wherein the copolymer contains from 0.15 to 0.3% by weight of said cross-linking agent.

11. A dispersion according to Claim 10, wherein the cross-linking agent is diallyl maleate or phthalate.

12. A dispersion according to any one of the preceding claims, wherein the copolymer contains from 25—38% of copolymerized methacrylic acid.

13. Dispersions according to Claim 1 or 9, as the case may be, being those compositions described in the foregoing examples.

14. An aqueous thickened composition obtained by addition to a dispersion according to any one of Claims 1—13, or such dispersion diluted with water, of an alkaline neutralizing agent in amount sufficient to neutralize some or all of the carboxylic acid groups in the copolymer and thereby provide a thickening effect.

15. A method of thickening an aqueous medium which comprises adding a copolymer dispersion according to any one of Claims 1—12, or such dispersion diluted with water, to the aqueous medium and adding an alkaline neutralizing agent to neutralize some or all of the carboxylic acid groups in the copolymer, the amount of copolymer dispersion added and the degree of neutralization of the carboxylic acid groups being such as to thicken the aqueous medium.

16. A method according to Claim 15, in which at least part of the alkaline neutralizing agent is introduced into the medium to be thickened before the addition of the copolymer dispersion.

17. A method according to Claim 15, in which the alkaline neutralizing agent is introduced to the medium to be thickened after the addition of the copolymer dispersion.

18. A process according to any one of Claims 15—17, in which the medium to be thickened is an aqueous dispersion of an emulsion polymer.

19. A method according to any one of

Claims 15—17, in which the medium to be thickened is an aqueous pigment suspension.

20. A method according to any one of Claims 15—17, in which the medium to be thickened is an aqueous clay suspension.

21. A method according to any one of Claims 15—20, wherein the amount of copolymer dispersion added is such as to provide 0.1% to 5% by weight of copolymer based on the total weight of solids in the first thickened medium.

22. A method according to any one of Claims 15—21, wherein all the carboxylic acid groups in the copolymer are neutralized.

23. A method according to any one of Claims 15—21, wherein from 50 to about 75% of the carboxylic acid groups in the copolymer are neutralized.

24. A method according to Claim 15, carried out substantially as hereinbefore described with reference to any of those of the foregoing examples which are appropriate.

25. A thickened aqueous medium when prepared by a method as claimed in any one of Claims 15—24.

26. A process in which an organic polar solvent system is thickened by the addition of a dispersion as claimed in any one of Claims 1—12 with or without neutralization of the carboxylic acid groups in the copolymer.

27. A powdered composition obtained by the removal of water from a dispersion as claimed in any one of Claims 1—12.

28. The method which comprises coating a substrate with an aqueous solution, obtained by adding ammonium hydroxide and a zinc ammonium complex salt to a dispersion according to any one of Claims 1—12, and drying the coating.

29. A method of conditioning an alkaline soil which comprises treating the soil with a dispersion according to any of Claims 1—12 after dilution of the latter with water.

30. The method of floc-stabilizing an aqueous suspension of solid material which comprises adding to the suspension a dispersion according to any of Claims 1—12, the carboxylic acid groups in the copolymer being at least partly neutralized before or after addition to the suspension.

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